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THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS ***US60/622,188***

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

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Additional inventors are being named on the ____ *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max):

FUNCTIONALIZED POLYMER WITH LINKING GROUP

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ENCLOSED APPLICATION PARTS (*check all that apply*)

☑ Specification *Number of Pages* 34

☐ Drawing(s) *Number of Sheets* ____

☐ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number of CDs ____

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METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☐ A check or money order is enclosed to cover the filing fees.

☐ Payment by credit card. Form PTO-2038 is attached.

☑ The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 06-0925
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FILING FEE Amount ($) 160.00

☑ The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ____

SIGNATURE TRK[illegible] Date 10/26/04

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Docket Number: P3096US1A

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PROVISIONAL APPLICATION COVER SHEET
Additional Page

First Named Inventor	Yuan-Yong Yan	Docket Number	P03096US1A

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Number 2 of 2

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FEE TRANSMITTAL for FY 2005

Effective 10/01/2004. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 160.00

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	Yuan-Yong Yan
Examiner Name	
Art Unit	
Attorney Docket No.	P03096US1A

METHOD OF PAYMENT *(check all that apply)*

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1001	790	2001	395	Utility filing fee	
1002	350	2002	175	Design filing fee	
1003	550	2003	275	Plant filing fee	
1004	790	2004	395	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	160.00

SUBTOTAL (1) ($) 160.00

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

			Extra Claims		Fee from below		Fee Paid
Total Claims		-20** =		X		=	
Independent Claims		- 3** =		X		=	
Multiple Dependent						=	

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
1202	18	2202	9	Claims in excess of 20
1201	88	2201	44	Independent claims in excess of 3
1203	300	2203	150	Multiple dependent claim, if not paid
1204	88	2204	44	** Reissue independent claims over original patent
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($)

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FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	1053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for *ex parte* reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	430	2252	215	Extension for reply within second month	
1253	980	2253	490	Extension for reply within third month	
1254	1,530	2254	765	Extension for reply within fourth month	
1255	2,080	2255	1,040	Extension for reply within fifth month	
1401	340	2401	170	Notice of Appeal	
1402	340	2402	170	Filing a brief in support of an appeal	
1403	300	2403	150	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,370	2453	685	Petition to revive - unintentional	
1501	1,370	2501	685	Utility issue fee (or reissue)	
1502	490	2502	245	Design issue fee	
1503	660	2503	330	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17(q)	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	790	2809	395	Filing a submission after final rejection (37 CFR 1.129(a))	
1810	790	2810	395	For each additional invention to be examined (37 CFR 1.129(b))	
1801	790	2801	395	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify) ____________

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($)

SUBMITTED BY

(Complete *(if applicable)*)

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EXPRESS MAIL CERTIFICATE

Title of the invention	FUNCTIONALIZED POLYMER WITH LINKING GROUP
Applicant(s):	Yuan-Yong Yan, et al.
Serial No.	
Filing Date:	
Examiner:	
Group Art Unit:	
Attorney Docket No.	P03096US1A
Filed with the following Office:	United States Patent and Trademark Office (USPTO)

Documents Enclosed:

Express Mail Certificate
34 pages of a Provisional Patent Application, including 25 Claims and Abstract
Fee Transmittal FY 2005
Provisional Application for Patent Cover Sheet
Fee to Deposit Account
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Pursuant to 37 CFR 1.10 I certify that this Provisional Patent Application is being deposited on the date indicated below with the United States Postal Service "Express Mail Post Office to Addressee" service addressed to: Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450.

Express Mail Mailing Label No.	Signature of Person Mailing Application
EL163693500US	Millie Persin
Date of Deposit	
October 26, 2004	Millie Persin

FUNCTIONALIZED POLYMER WITH LINKING GROUP

BACKGROUND INFORMATION

1. Field of the Invention

The invention relates to the manufacture and use of functionalized polymers that are capable of interacting with fillers.

2. Background of the Invention

Tire treads, power belts, and the like often are made from compositions that contain one or more elastomers and one or more reinforcing materials such as, for example, particulate carbon black and silica. For a general discussion of this topic, see, e.g., *The Vanderbilt Rubber Handbook*, 13th ed. (1990), pp. 603-04.

Safety and durability considerations mandate that tire treads provide both good traction and resistance to abrasion; however, motor vehicle fuel efficiency concerns argue for a minimization in their rolling resistance, which correlates with a reduction in hysteresis and heat build-up during operation of the tire. The foregoing considerations are, to a great extent, competing and somewhat contradictory: a tire tread composition designed to improve tread traction on the road usually results in increased rolling resistance and vice versa.

Typically, filler(s), polymer(s), and additives are chosen so as to provide an acceptable compromise or balance of these properties. Ensuring that constituent reinforcing filler(s) are well dispersed throughout the elastomeric material(s) in such compositions both enhances processability and acts to improve physical properties such as, e.g., compound Mooney viscosity, elastic modulus, tan δ, and the like. Resulting articles made from such compositions can exhibit desirable properties such as reduced hysteresis, reduced rolling resistance, and good traction on wet pavement, snow and ice.

One way to improve dispersion of fillers is to increase their interaction with the elastomer(s). Examples of efforts of this type include high temperature mixing in the presence of selectively reactive promoters, surface oxidation of the compounding materials, surface grafting, and chemical modifications to the terminal ends of the polymers with, e.g., amines, tin compounds, and the like.

Because elastomers used in such compositions often are made via anionic polymerization techniques, attachment of certain functional groups, particularly

amines, is difficult. This is because living polymers are terminated by active hydrogen atoms such as are present in, e.g., hydroxyl groups, thiol groups, and particularly primary and secondary amine groups. This undesired termination can be avoided through use of reaction schemes that allow for attachment of a non-amine N-containing compound followed by conversion to an amine, i.e., indirect attachment schemes.

Continued hysteresis reduction and provision of a direct mechanism for attaching amine functionality to a living polymer both remain highly desirable.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a functionalized polymer that includes an elastomer with a terminal functional group including at least one heteroatom. Between the elastomer and the functional group is provided a unit that includes a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion.

In another aspect, the present invention provides a method of making a functionalized polymer that includes chemically bonding to a living polymer a unit that includes a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion, such that addition of the unit to the living polymer does not terminate the living polymer. A desired functional group may be added to the living polymer, or the polymer may be quenched without a functional group.

Other aspects of the present invention will be apparent to the ordinarily skilled artisan from the detailed description that follows.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

To assist in understanding that description of the invention, certain definitions are provided immediately below. These definitions apply hereinthroughout unless a contrary intention is explicitly indicated:

"polymer" means the polymerization product of one or more monomers and is inclusive of homo-, co-, ter-, tetra-polymers, etc.;

"polyene" means a compound with multiple carbon-to-carbon double bonds and includes dienes, trienes, etc.;

"mer unit" means that portion of a polymer derived from a single reactant molecule (e.g., an ethylene mer unit has the general formula $-CH_2CH_2-$);

"homopolymer" means a polymer consisting essentially of a single type of repeating mer unit;

"copolymer" means a polymer that includes mer units derived from two reactants (normally monomers) and is inclusive of random, block, segmented, graft, etc., copolymers;

"interpolymer" means a polymer that includes mer units derived from at least two reactants (normally monomers) and is inclusive of copolymers, terpolymers, tetrapolymers, and the like;

"macromolecule" means an oligomer or polymer;

"terminus" means an end of a constituent chain of a macromolecule;

"terminal moiety" means that portion of a molecule located at its terminus;

"radical" means the portion of a molecule that remains after reacting with another molecule;

"chemically bonded" means attached through a bond that is covalent or ionic;

"secondary amino radical ion" means an anion having the general formula $R^1R^2N^-$ where R^1 and R^2 independently are alkyl, aryl, alkenyl, etc., hydrocarbon-containing chains with the proviso that one or both of R^1 and R^2 can be polymeric;

"heteroatom" means an atom other than carbon or hydrogen; and

"hysteresis" means the difference between the energy applied to deform an article made from an elastomeric compound and the energy released as the article returns to its initial, non-deformed state.

The functionalized polymer includes a polymeric chain with a terminal functional group including at least one heteroatom and an intermediate unit, as represented by the formula:

$$E\text{-}A\text{-}G_t$$

where E is an elastomer, G_t is a terminal functional group comprising at least one heteroatom, and A is an intermediate unit comprising a terminal moiety which, in its anionic form is less basic than a secondary amino radical ion. Those of ordinary skill in the chemical arts are familiar with relative basicities and, accordingly, are aware of those atoms that can be present in the type of terminal moiety just described. A terminal moiety which, in its anionic form has a pK_a greater than the pK_a of a secondary amino radical ion is less basic than a secondary amino radical ion. For the sake of example only, two relatively common examples of such heteroatoms are O and S.

Each of the portions of the functionalized polymer now will be described separately and in detail.

The polymeric chain preferably is elastomeric. Accordingly, it can include mer units that include unsaturation, which can be mer units derived from polyenes, particularly dienes and/or trienes (e.g., myrcene). Preferred dienes include C_4-C_{12} dienes. Particularly preferred are conjugated dienes such as, but not limited to, 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and 1,3-hexadiene. Homo- and co-polymers that include just diene-derived mer units constitute one preferred type of elastomer.

The polymeric chain also can include mer units derived from vinyl aromatics, particularly the C_8-C_{20} vinyl aromatics such as, e.g., styrene, α-methyl styrene, *p*-methyl styrene, the vinyl toluenes, and the vinyl naphthalenes. When used in conjunction with one or more dienes, the vinyl aromatic-derived mer can constitute from about 1 to about 50% by wt., preferably from about 10 to about 45% by wt., and more preferably from about 20 to about 35% by wt., of the polymer chain. Interpolymers of diene(s) and vinyl aromatic(s) constitute another preferred type of elastomer. Especially when such interpolymers are to be used in applications such as tire treads, the resulting interpolymers preferably are random in nature, i.e., the mer units derived from each type of constituent monomer preferably do not form blocks and, instead, are incorporated in a non-repeating, essentially simultaneous, generally random manner.

Particularly preferred elastomers include poly(butadiene), (poly)isoprene (either natural or synthesized), and interpolymers of butadiene and styrene such as, e.g., copoly(styrene/butadiene) also known as SBR.

Dienes can incorporate into polymeric chains in more than one way. Especially for tire tread applications, controlling the manner in which the diene mer units are incorporated into the polymer (i.e., the 1,2-microstructure of the polymer) can be desirable. Based on total diene content, a polymer chain preferably has an overall 1,2-microstructure of from about 10 to about 80%, more preferably of from about 25 to 65%.

The number average molecular weight (M_n) of the polymer preferably is such that a quenched sample will exhibit a gum Mooney viscosity (ML_4 / 100°C) of from about 2 to about 150.

A preferred technique for making the subject polymers is solution polymerization . An alternative technique for making the subject polymers is emulsion polymerization.

Solution polymerization typically involves an initiator. Exemplary initiators include organolithium compounds, particularly alkyllithium compounds. Preferred organolithium initiators include N-lithio-hexamethyleneimine; n-butyllithium; tributyltin lithium; dialkylaminolithium compounds such as dimethylaminolithium, diethylaminolithium, dipropylaminolithium, dibutylaminolithium and the like; dialkylaminoalkyllithium compounds such as diethylaminopropyllithium; and those trialkyl stanyl lithium compounds involving C_1-C_{12}, preferably C_1-C_4, alkyl groups.

In addition to the organolithium initiators, also useful are the so-called functionalized initiators that become incorporated into the polymer chain, thus providing a functional group at the initiated end of the chain. Examples of such materials include the reaction product of organolithium compounds and, for example, N-containing organic compounds (e.g., substituted aldimines, ketimines, secondary amines,) optionally pre-reacted with a compound such as diisopropenyl benzene. A more detailed description of these materials can be found in, e.g., U.S. Pat. Nos. 5,153,159 and 5,567,815, both of which are hereby incorporated by reference.

Useful anionic polymerization solvents include the various C_5-C_{12} cyclic and acyclic alkanes, their alkylated derivatives, and mixtures thereof.

As mentioned previously, the mer units of the polymer preferably are incorporated randomly. In solution polymerizations, randomization as well as vinyl content (i.e., 1,2-microstructure) can be increased through use of a coordinator, usually a polar compound, in the polymerization ingredients. Up to 90 or more equivalents of coordinator can be used per equivalent of initiator, with the amount depending on, e.g., the amount of vinyl content desired, the level of non-diene monomer employed, the reaction temperature, and the nature of the specific coordinator employed. Compounds useful as coordinators include organic compounds having an O or N heteroatom and a non-bonded pair of electrons. Examples include dialkyl ethers of mono- and oligo-alkylene glycols; crown ethers; tertiary amines such as tetramethylethylene diamine; THF; THF oligomers; linear and cyclic oligomeric oxolanyl alkanes such as 2,2'-di(tetrahydrofuryl) propane, di-piperidyl ethane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, diethyl ether, tributylamine, oligomeric oxolanyl propanes (OOPs) and the like. Details of linear and cyclic oligomeric oxolanyl coordinators can be found in U.S. Pat. No. 4,429,091, the teaching of which relating to the manufacture and use of such materials is incorporated by reference herein.

Although the ordinarily skilled artisan understands the type of conditions typically employed in solution polymerization, a representative description is provided for the sake of convenience to the reader. This representative description is based on a batch polymerization, although the ordinary skilled artisan easily can extend this to other processes such as semi-batch and continuous.

Polymerization typically begins by charging a blend of the monomer(s) and solvent to a reaction vessel, followed by addition of the coordinator (if used) and initiator, which often are added as part of a solution or blend; alternatively, the monomer(s) and coordinator can be added to the initiator. The procedure preferably is carried out under anhydrous, anaerobic conditions. The reactants can be heated to a temperature of up to about 150°C and agitated. After a desired degree of conversion has been reached, the heat source (if used) is removed and, if no functionalization of the polymer is desired, the resulting polymer is removed

from the reaction vessel and/or quenched. Quenching typically is conducted by stirring the polymer in an active H-containing compound (e.g., an alcohol) for up to about 120 minutes at temperatures of from about 30° to 150°C. Thereafter, solvent is removed by conventional techniques such as drum drying, extruder drying, vacuum drying or the like, which may be combined with coagulation with water, alcohol or steam, thermal desolvation, etc. (If coagulation is performed, oven drying may be desirable.)

To make a functionalized polymer, the polymer is provided with a functional group prior to its quenching. In the present invention, this functionalization is preceded by the introduction of what has been referred to herein as an intermediate unit. This unit is discussed in more detail below.

Many classes of compounds can be used to provide the intermediate unit. Each compound provides a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion. Secondary amino radical ions are themselves less basic than carbanions; however, both secondary amino radical ions and carbanions are sufficiently basic that active hydrogens of the type present when amine-containing compounds are introduced terminate the amino radical ions and carbanions.

Examples of ions that are less basic than secondary amino radical ions include, but certainly are not limited to, $-O^-$ and $-S^-$. This is convenient because compounds that contain O and S are plentiful, thus providing the ordinarily skilled artisan with a wide range of useful materials from which to choose.

A convenient method of delivering this type of terminal moiety to a polymer chain involves the introduction of a heteroatom-containing cyclic compound into a system that contains a living polymer. The conditions used to provide the living polymer typically are adequate to open the ring of the cyclic structure and allow the resulting radical to attach to the polymer. This added radical, referred to above as an intermediate unit, has a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion.

Examples of heteroatom-containing cyclic compounds include, but are not limited to, cyclic siloxanes, epoxides, and the S-containing analogs of each. Examples of S-containing analogs are cyclohexene sulfide and propylene sulfide.

Of the siloxanes, preferred are those that can deliver up to 6, preferably 3 to 4, repeating polysiloxane units. Also preferred are those where at least some, preferably each, of the Si atoms are substituted with a C_1-C_6 substituent, preferably a C_1-C_3 alkyl group. Particularly preferred due to availability and cost are hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.

With respect to the epoxides and episulfides, a wide range of commercially available materials can be utilized; examples of such materials include various alkylene oxides and sulfides such as butylene oxide, various cycloalkene oxides and sulfides such as cyclohexene oxide, and 3-glycidoxypropyltrimethoxysilane, 1,2 epoxybutane, and ethylene oxide, preferred are those materials with boiling points that are sufficiently high so as to remain liquid at temperatures commonly encountered during solution polymerizations. The intermediate unit resulting from the use of the epoxide or episulfide can be aliphatic or cyclic. This type of material can result in intermediate units that connect to the polymer chains by a carbon-to-carbon bond.

No particularly unusual reaction conditions or sequences are believed to be necessary to attach such intermediate units, although exemplary reaction conditions can be found below in the examples; reaction temperature for attachment of the intermediate unit generally range between 45^0C and 80^0C, and preferably between 50^0C and 72^0C. Generally the compound(s) used to provide the intermediate unit is added in amounts so as to provide, on average, no more than two intermediate units per living polymer and preferably no more than one intermediate unit per living polymer. In one embodiment, the amount of compound(s) used to provide the intermediate unit is such that the mole ratio of intermediate unit to functional group is from about 1:1 to 1:6. In another embodiment the amount of compound(s) used to provide the intermediate unit is such that the mole ratio of intermediate unit to functional group is about 1:3.

In one particular embodiment, the intermediate unit preferably constitutes a relatively minor proportion of the overall macromolecule; in general, its molecular weight typically is no more than about 400 g/mol, preferably no more than about 360 g/mol, more preferably no more than about 340 g/mol, and most preferably no more than 320 g/mol.

As mentioned above, the terminal moiety of the resulting intermediate unit, in its anionic form, is less basic than a secondary amino radical ion. This allows the resulting anion to react with a functional group. The functional group includes a sub-group that can react with the terminal moiety, and a second sub-group that may react with another molecule present such as a filler in a tire compound. Examples of such second sub-groups are heteroatom-containing functional groups that have an active hydrogen atom attached to the heteroatom which, otherwise, would tend to terminate the living polymers.

The living polymer with an intermediate unit is then functionalized with a terminal functional group comprising at least one heteroatom. The terminal functional group is preferably a heteroatom-containing functional group. Some examples of heteroatom-containing functional groups are alkoxysilanes, halogen-containing compounds, acetic anhydride, 4-methylbenzoic acid anhydride, methyl succinic anhydride, 4-methylphyl-succinic anhydride, 1,4-butane sultone, and 2-dodecen-1-ylsuccinic anhydride.

Examples of compounds from which such functional groups can be derived include, but are not limited to:

alkoxysilanes include but are not limited to: methyltrimethoxysilane, tetraethylorthosilicate, 3-aminopropyltriethoxysilane, N-(3-triethoxy-silylpropyl)-4,5-dihydroimidazole (TEOSI), 3-isocyanatopropyltriethoxysilane, n-methylaminopropylmethyldimethoxysilane, n-methylaminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, and $C_{15}H_{33}NSiO_3$ (available as S340 from Sigma-Aldrich Co.; St. Louis, Missouri);

halogen-containing compounds include, but are not limited to: silicone tetrachloride, tin tetrachloride, acetyl chloride, p-toluoyl chloride, methanesulfonyl chloride, p-toluoyl sulfonyl chloride, haloalkylamines such as 3-bromopropylamine, 3-chloropropylamine, 3-(2-bromoethyl)indole, n-methyl-3-bromopropylamine, 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, chlorotrimethylsilane, dichlorodimethylsilane, and trichloromethylsilane;

anhydrides such as acetic anhydride, 4-methylbenzoic acid anhydride, methyl succinic anhydride, 4-methylphenyl-succinic anhydride, and 2-dodecen-1-yl succinic anhydride;

and O- and S-containing compounds such as 1,4-butane sulfone, and the like.

The functionalized polymer can be utilized in a tread stock compound or can be blended with any conventionally employed tread stock rubber which includes natural rubber and/or non-functionalized synthetic rubbers such as, e.g., one or more of poly(isoprene), SBR, poly(butadiene), butyl rubber, neoprene, ethylene/propylene rubber (EPR), ethylene/propylene/diene rubber (EPDM), acrylonitrile/butadiene rubber (NBR), silicone rubber, fluoroelastomers, ethylene/acrylic rubber, ethylene/vinyl acetate interpolymer (EVA), epichlorohydrin rubbers, chlorinated polyethylene rubbers, chlorosulfonated polyethylene rubbers, hydrogenated nitrile rubber, tetrafluoroethylene/propylene rubber and the like. When a functionalized polymer(s) is blended with conventional rubber(s), the amounts can vary from about 5 to about 99% by wt. of the total rubber, with the conventional rubber(s) making up the balance of the total rubber. The minimum amount depends largely on the degree of reduced hysteresis desired.

Amorphous silica (SiO_2) can be utilized as a filler. Silicas are generally classified as wet-process, hydrated silicas because they are produced by a chemical reaction in water, from which they are precipitated as ultrafine, spherical particles. These primary particles strongly associate into aggregates, which in turn combine less strongly into agglomerates. "Highly dispersible silica" is any silica having a very substantial ability to de-agglimerate and to disperse in an elastomeric matrix, which can be observed by thin section microscopy. The surface area gives a reliable measure of the reinforcing character of different silicas. The Brauner, Emmet and Teller ("BET") method (described in *J. Am. Chem. Soc.*, vol. 60, p. 309 et seq.) is a recognized method for determining surface area. The BET surface area of silicas preferably is less than 450 m^2/g, more preferably from about 32 m^2/g to about 400 m^2/g, more preferably from about 100 m^2/g to about 250 m^2/g, and most preferably from about 150 m^2/g to about 220 m^2/g. The pH of the silica filler

is generally from about 5 to about 7 or slightly over, preferably from about 5.5 to about 6.8.

Some commercially available silicas which may be used include Hi-Sil™ 215, Hi-Sil™ 233, and Hi-Sil™ 190 (PPG Industries, Inc.; Pittsburgh, Pennsylvania). Other suppliers of commercially available silica include Degussa Corp. (Parsippany, New Jersey), Rhodia Silica Systems (Cranbury, New Jersey), and J.M. Huber Corp. (Edison, New Jersey).

Silica can be employed in the amount of about 1 to about 100 parts by weight (pbw) per 100 parts of polymer (phr), preferably in an amount from about 5 to about 80 phr. The useful upper range is limited by the high viscosity imparted by fillers of this type.

Other useful fillers include all forms of carbon black including, but not limited to, furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace blacks, high abrasion furnace blacks, fast extrusion furnace blacks, fine furnace blacks, intermediate super abrasion furnace blacks, semi-reinforcing furnace blacks, medium processing channel blacks, hard processing channel blacks, conducting channel blacks, and acetylene blacks; mixtures of two or more of these can be used. Carbon blacks having a surface area (EMSA) of at least 20 m^2/g, preferably at least about 35 to about 200 m^2/g or higher are preferred; surface area values can be determined by ASTM D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. The carbon blacks may be in pelletized form or an unpelletized flocculent mass, although unpelletized carbon black can be preferred for use in certain mixers.

The amount of carbon black can be up to about 50 phr, with about 5 to about 40 phr being typical. When carbon black is used with silica, the amount of silica can be decreased to as low as about 1 phr; as the amount of silica decreases, lower amounts of the processing aids, plus silane if any, can be employed.

Elastomeric compounds typically are filled to a volume fraction, which is the total volume of filler(s) added divided by the total volume of the elastomeric stock, of about 25%; accordingly, typical (combined) amounts of reinforcing fillers, i.e., silica and carbon black, is about 30 to 100 phr. In certain preferred embodiments, compositions that include the functionalized polymer of the present

invention can include carbon black as the primary filler (i.e., a majority of the filler is carbon black) or the only filler.

When silica is employed as a reinforcing filler, addition of a coupling agent, such as silane, is customary so as to ensure good mixing in, and interaction with, the elastomer(s). Generally, the amount of silane that is added ranges between about 4 and 20% by weight, based upon the weight of silica filler present in the elastomeric compound.

Coupling agents can have a general formula of Z-T-X, in which Z represents a functional group capable of bonding physically and/or chemically with a group on the surface of the silica filler (e.g., surface silanol groups); T represents a hydrocarbon group linkage; and X represents a functional group capable of bonding with the elastomer (e.g., via a S-containing linkage). Such coupling agents include organosilanes, in particular polysulfurized alkoxysilanes (see, e.g., U.S. Pat. Nos. 3,873,489, 3,978,103, 3,997,581, 4,002,594, 5,580,919, 5,583,245, 5,663,396, 5,684,171, 5,684,172, 5,696,197, etc.) or polyorganosiloxanes bearing the X and Z functionalities mentioned above. One preferred coupling agent is bis[3-(triethoxysilyl)propyl]tetrasulfide.

Additionally, a processing aid can be used to reduce the amount of silane employed. See, e.g., U.S. Pat. No. 6,525,118 for a description of fatty acid esters of sugars used as processing aids. Additional fillers useful as processing aids include, but are not limited to, mineral fillers, such as clay (hydrous aluminum silicate), talc (hydrous magnesium silicate), and mica as well as non-mineral fillers such as urea and sodium sulfate. Preferred micas contain principally alumina, silica and potash, although other variants are also useful, as set forth below. The additional fillers can be utilized in an amount of up to about 40 phr, preferably up to about 20 phr.

Other conventional rubber additives also can be added. These include, for example, plasticizers, antioxidants, curing agents and the like.

All of the ingredients can be mixed using standard equipment such as, e.g., Banbury or Brabender mixers

Reinforced rubber compounds conventionally are cured with about 0.2 to about 5 phr of one or more known vulcanizing agents such as, for example, sulfur

or peroxide-based curing systems. For a general disclosure of suitable vulcanizing agents, the interested reader is referred to an overview such as that provided in Kirk-Othmer, *Encyclopedia of Chem. Tech.*, 3d ed., (Wiley Interscience, New York, 1982), vol. 20, pp. 365-468.

The following non-limiting, illustrative examples provide the reader with detailed conditions and materials that can be useful in the practice of the present invention.

EXAMPLES

For all examples, a dried glass vessel previously sealed with extracted septum liners and perforated crown caps under a positive N_2 purge was used for all preparations. Butadiene in hexane (22.5% by weight butadiene), styrene in hexane (33% by wt. styrene), hexane, n-butyllithium (1.7 M in hexane), oligomeric oxolanyl propanes ("OOPs") (1.6 M solution in hexane, stored over CaH_2), and BHT solution in hexane were used. Commercially available reagents and starting materials included the following, all of which were used without further purification unless otherwise noted:

- from ACROS Organics (Geel, Belgium): methyltrimethoxysilane, tetraethyl orthosilicate, 3-aminopropyltriethoxysilane, hexamethylcyclotrisiloxane , and octamethylcyclotetrasiloxane , with the cyclic siloxanes being dried over CaH_2 prior to use;
- from Sigma-Aldrich Co. (St. Louis, Missouri): $SiCl_4$ and $SnCl_4$
- from Gelest, Inc. (Morrisville, Pennsylvania): N-(3-triethyoxy-silylpropyl)-4,5-dihydroimidazole (TEOSI), 3-isocyanatopropyltriethoxysilane, N-methylamino-propylmethyldimethoxysilane, N-methylaminopropyltrimethoxysilane.

Data corresponding to "50°C Dynastat tan δ" were acquired from tests conducted on a Dynastat™ mechanical spectrometer (Dynastatics Instruments Corp.; Albany, New [redacted] Hz frequency. Data corresponding to "Surfanalyzer D.I." were acquired from tests conducted on a Surfanalyzer™ surface profilometer (Federal Products Co.; Providence, Rhode Island).

Examples 1-3: *Standard initiator (n-BuLi)*

For Examples 1-3, a batch of polymer was prepared using a standard initiator, and from this batch, three samples were taken and reacted with different compounds. To a 7.6 L, N_2-purged reactor equipped with a stirrer was added 1.47 kg hexane, 0.41 kg styrene (in hexane), and 2.60 kg butadiene (20.9% by wt. in hexane). The reactor was charged with 3.68 mL n-BuLi (in hexane), followed by 1.18 mL of 1.6M OOPS (in hexane). The reactor jacket was heated to 50°C and, after 22 minutes, the batch temperature peaked at 65.6°C. After an additional 10 minutes, the polymer cement was removed from the reactor and stored in separate 0.83 L dried glass vessels.

Three of these samples were used as Examples 1-3. Examples 1-3 were separately reacted. Example 1 was reacted with N,N-TMS-aminopropyltriethoxysilane in a 50°C bath for 30 minutes. Example 2 was reacted with hexamethylcyclotrisiloxane (1.0 M in hexane) in a 50°C bath for 30 minutes. Example 3 was quenched with isopropanol in a 50°C bath for 30 minutes. Each was coagulated in isopropanol containing butylated hydroxy toluene (BHT) and drum dried to yield polymers with the properties as shown in Table 2.

Examples 4-5: *Functional initiator (DAPDT)*

For Examples 4-5, polymerization batch was prepared using a functional initiator, from which two separate samples were taken. The polymers in the two samples were reacted with different compounds. To a 7.6 L, N_2-purged reactor equipped with a stirrer was added 1.47 kg hexane, 0.41 kg styrene (33% by weight in hexane), and 2.60 kg butadiene (20.9% by wt. in hexane). The reactor was charged with a mixture of 1.48 g 2-(4-dimethylamino)phenyl-1,3-dithiane in 10 mL THF and 1 mL triethylamine and 3.68 mL n-BuLi (1.7 M in hexane), and the contents were agitated at 24°C for 5 minutes before addition of 1.04 mL OOPS (1.6 M in hexane). The reactor jacket was heated to 50°C and, after 18.4 minutes, the batch temperature peaked at 71.2°C. After an additional 10 minutes, the polymer cement was removed from the reactor and stored in separate 0.83 L dried glass vessels. Examples 4 and 5 were held in separate vessels.

Two of these samples were used as Examples 4 and 5. Examples 4 and 5 were then separately reacted. Example 4 was reacted with

hexamethylcyclotrisiloxane (1.0 M in hexane) in a 50° C bath for 30 minutes. Example 5 was quenched with isopropanol in a 50°C bath for 30 minutes. Each was coagulated with isopropanol containing butylated hydroxyl toluene (BHT) and drum dried to yield polymers with the properties shown in Table 2.

The samples prepared in Examples 1-5 were used to prepare vulcanizable elastomeric compounds containing reinforcing fillers. The formulation for these compounds is shown in Table 1.

Table 1: Compound formulation

Masterbatch	Amount (phr)
Polymer	100
Silica	30
carbon black	35
Antiozonant	0.95
stearic acid	1.5
LVA oil	10
Re-mill	
60% Si75 on 22.5% wax + 17.5% binder	4.57
Final	
ZnO	2.5
Sulfur	1.7
accelerator (CBS)	1.5
PVI	0.25
accelerator (DPG)	0.5
TOTAL	188.47

Results of physical testing on these compounds are shown below in Table 2. From this data, a reinforced SBR polymer having a hexamethylcyclotrisiloxane-derived unit attached (Examples 2 and 4) can be seen to provide a greater than 30% reduction in tan δ at 50°C strain sweep, compared to a control polymer, regardless of the type of initiator used. A TMS-protected aminopropyltriethoxysilane-reacted polymer (Example 1) showed a slight reduction in tan δ compared to its base polymer (Example 3).

Table 2: Physical testing data from Examples 1-5

	1	2	3 (control)	4	5 (control)
M_n (kg/mol)	104	102	102	120	115
M_w / M_n	1.17	1.03	1.04	1.08	1.04
% coupling	8.2	0.0	0.0	7.2	8.9
T_g (°C)	-36.4	-37.1	-36.0	-38.4	-38.0
Surfanalyzer D.I.	86.3	86.1	84.4	91.6	89.7
171°C MDR t_{50} (min)	7.2	6.6	6.3	5.8	5.21
171°C MH-ML (kg-cm)	20.8	15.4	22.8	17.5	24.51
ML_{1+4} @130°C	53.3	78.8	49.9	*ND*[1]	70.0
300% modulus @ 23°C (MPa)	8.3	11.5	8.1	12.9	10.5
Tensile strength @ 23°C (MPa)	12.6	15.3	11.2	18.3	14.8
Temp. sweep 0°C tan δ	0.181	0.228	0.177	0.229	0.182
Temp. sweep 50°C tan δ	0.234	0.203	0.241	0.162	0.211
RDA 0.25-14% ΔG' (MPa)	7.359	0.209	7.872	1.932	6.235
50°C RDA strain sweep (5% strain) tan δ	0.2352	0.1725	0.2606	0.1398	0.2068
50°C Dynastat tan δ	0.2105	0.1656	0.2111	0.1394	0.1864

[1]*Not determined. Initial surge in property exceeded pre-set limit for testing device.*

Examples 6-24: *Functionalized polymers with a hexamethlcyclotrisiloxane intermediate group*

Using essentially the same procedure described for Examples 1-5, a N_2-purged reactor equipped with a stirrer was charged with hexane, styrene, and butadiene. The reactor was charged with n-BuLi, followed by OOPs. The reactor jacket was heated and, after 20-30 minutes, the batch temperature peaked at 10-15°C above the jacket temperature. After an additional about 10 minutes, the polymer cement was removed from the reactor and stored in separate dried glass vessels. Examples 6-24 were held in separate vessels.

In a 50°C bath for about 30 minutes, some of the samples were reacted with hexamethylcyclotrisiloxane to provide an intermediate unit, followed by reacting some of the samples with a functionalizing agent, followed by quenching with isopropanol, according to Table 3.

Table 3: Reaction and termination of Examples 6-24

Example	A (Intermediate Unit)	G_t (Functionalizing Agent)	Quenching Agent
6	N/A	N/A	isopropanol
7	hexamethylcyclotrisiloxane	N/A	isopropanol
8	hexamethylcyclotrisiloxane	methyltrimethoxysilane	isopropanol
9	hexamethylcyclotrisiloxane	3-aminopropyltriethoxysilane	isopropanol
10	hexamethylcyclotrisiloxane	TEOSI	isopropanol
11	hexamethylcyclotrisiloxane	S340	isopropanol
12	N/A	N/A	isopropanol
13	hexamethylcyclotrisiloxane	N/A	isopropanol
14	hexamethylcyclotrisiloxane	3-aminopropyltrimethoxysilane	isopropanol
15	hexamethylcyclotrisiloxane	[3-(methylamino)propyl]trimethoxysilane	isopropanol
16	hexamethylcyclotrisiloxane	2-dodecen-1-yl succinic anhydride	isopropanol
17	hexamethylcyclotrisiloxane	1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane	isopropanol
18	N/A	N/A	isopropanol
19	hexamethylcyclotrisiloxane	N/A	isopropanol
20	hexamethylcyclotrisiloxane	3-aminopropyltriethoxysilane	isopropanol
21	hexamethylcyclotrisiloxane	3-aminopropyltrimethoxysilane	isopropanol
22	hexamethylcyclotrisiloxane	N-[3-(trimethoxysilyl)propyl]ethylenediamine	isopropanol
23	hexamethylcyclotrisiloxane	[3-(methylamino)propyl]trimethoxysilane	isopropanol
24	N/A	benzosulfimide	isopropanol

Each Example was coagulated, drum dried, and compounded substantially as in Examples 1-5 to yield polymers and vulcanizable compositions with properties as shown in Table 4 (Examples 6-11), Table 5 (Examples 12-17), and Table 6 (Examples 18-24). For those rows that include two data points, the upper is for a formulation with carbon black as the sole filler, and the lower is for a formulation in which a blend of carbon black and silica filler was used.

Table 4: Testing data from Examples 6-11

	6	7	8	9	10	11
M_n (kg/mol)	98	95	100	108	105	105
M_w / M_n	1.05	1.02	1.08	1.16	1.14	1.13
% coupling	4.8	0.0	10.2	21.2	15.5	15.5
T_g (°C)	-35.9	-38.1	-37.7	-37.4	-38.1	-37.5
Bound rubber (%)	--	7.7 67.5	11.7 66.0	24.4 68.1	19.9 63.0	22.7 67.3
Surfanalyzer D.I.	--	95.0 92.9	93.7 89.4	97.0 88.8	97.0 84.6	96.9 83.9
171°C MDR t_{50} (min)	--	2.87 7.19	3.20 6.83	2.49 7.01	2.79 8.43	2.65 6.62
171°C MH-ML (kg-cm)	--	17.1 16.0	15.5 16.8	15.4 15.4	16.4 14.9	17.8 15.9
ML_{1+4} @ 130°C	--	16.6 74.6	19.9 72.5	23.4 72.3	23.4 70.4	23.3 73.8
300% modulus @ 23°C (MPa)	--	10.2 11.7	8.9 12.5	10.4 11.8	10.2 10.2	12.0 11.8
Tensile strength @ 23°C (MPa)	--	16.1 15.3	16.2 14.0	18.3 16.2	14.4 17.1	17.3 14.8
Temp. sweep 0°C tan δ	--	0.334 0.244	0.342 0.252	0.335 0.238	0.337 0.236	0.353 0.238
Temp. sweep 50°C tan δ	--	0.263 0.182	0.265 0.193	0.250 0.187	0.250 0.195	0.244 0.190
RDA 0.25-14% ΔG′ (MPa)	--	4.968 2.113	4.869 2.196	2.941 1.822	3.210 1.903	4.289 1.974
50°C RDA strain sweep (5% strain) tan δ	--	0.2684 0.1883	0.2820 0.1786	0.2273 0.1779	0.2353 0.1873	0.2365 0.1790
50°C Dynastat tan δ	--	0.2581 0.1762	0.2635 0.1725	0.2069 0.1763	0.2150 0.1771	0.2055 0.1751

Table 5: Testing data from Examples 12-17

	12	13	14	15	16	17
M_n (kg/mol)	97	99	92	95	103	100
M_w / M_n	1.03	1.05	1.10	1.08	1.08	1.06
% coupling	0.0	5.0	8.7	8.9	11.5	6.8
T_g (°C)	-36.9	-36.8	-36.1	-37.0	-37.2	-36.4
Bound rubber (%)	10.7 15.9	12.5 63.8	32.9 71.1	24.1 73.2	14.2 19.5	11.5 13.9
Surfanalyzer D.I.	91.9 71.4	90.3 64.3	95.2 61.3	97.5 58.2	97.0 66.3	97.5 62.6
171°C MDR t_{50} (min)	2.96 7.67	2.90 7.24	2.81 7.04	2.74 6.47	2.53 6.09	3.00 7.37
171°C MH-ML (kg-cm)	16.7 23.0	17.9 16.0	15.5 16.4	16.8 15.3	16.7 16.6	17.5 16.5
ML_{1+4} @ 130°C	19.9 56.3	21.0 81.9	27.8 90.0	25.0 91.6	23.7 80.2	21.3 80.2
300% modulus @ 23°C (MPa)	10.3 9.9	11.2 14.6	11.5 16.5	11.0 14.4	9.9 14.7	10.8 14.6
Tensile strength @ 23°C (MPa)	17.1 12.6	18.0 14.5	17.9 16.3	17.7 14.5	16.1 15.6	16.5 16.3
Temp. sweep 0°C tan δ	0.201 0.165	0.199 0.235	0.205 0.242	0.200 0.235	0.196 0.234	0.202 0.240
Temp. sweep 50°C tan δ	0.274 0.225	0.273 0.190	0.258 0.174	0.268 0.182	0.271 0.196	0.271 0.185
RDA 0.25-14% ΔG' (MPa)	4.959 9.461	4.816 2.629	2.397 2.628	3.721 2.793	4.540 2.812	4.601 2.570
50°C RDA strain sweep (5% strain) tan δ	0.2862 0.2472	0.2685 0.1855	0.2136 0.1825	0.2372 0.1827	0.2574 0.1677	0.2583 0.1697
50°C Dynastat tan δ	0.2644 0.2224	0.2457 0.1816	0.2035 0.1726	0.2193 0.1733	0.2559 0.1718	0.2390 0.1628

Table 6: Testing data from Examples 18-24

	18	19	20	21	22	23	24
M_n (kg/mol)	107	101	102	104	92	103	98
M_w / M_n	1.06	1.06	1.16	1.27	1.10	1.08	1.05
% coupling	0	0	6.53	8.22	4.26	0	0
T_g (°C)	-35.6	-37.2	-37.1	-37.1	-37.0	-37.1	-37.0
Bound rubber (%)	11.5 18.2	--	29.3 80.1	30.2 82.8	28.8 83.9	25.9 82.9	11.7 76.8
Surfanalyzer D.I.	95.1 80.0	--	95.1 67.1	94.1 65.1	94.2 76.4	95.3 64.5	93.9 77.2
171°C MDR t_{50} (min)	2.80 7.38	--	2.62 6.92	2.54 6.67	2.49 5.53	2.41 5.85	3.11 6.96
171°C MH-ML (kg-cm)	18.0 23.2	--	16.9 14.6	16.1 14.8	15.9 15.3	17.6 15.4	17.1 14.8
ML_{1+4} @ 130°C	26.8 66.7	--	30.0 97.1	30.3 97.6	29.0 99.5	29.0 98.5	23.2 72.5
300% modulus @ 23°C (MPa)	10.8 9.6	--	11.2 13.6	10.9 13.3	10.4 14.7	12.0 13.1	10.3 12.0
Tensile strength @ 23°C (MPa)	17.1 13.8	--	16.3 18.0	17.7 17.2	17.9 15.8	19.1 16.5	17.3 17.4
Temp. sweep 0°C tan δ	0.214 0.200	--	0.215 0.258	0.220 0.268	0.203 0.262	0.208 0.263	0.192 0.267
Temp. sweep 50°C tan δ	0.262 0.232	--	0.249 0.191	0.253 0.183	0.249 0.186	0.247 0.184	0.275 0.197
RDA 0.25-14% ΔG′ (MPa)	5.187 8.992	--	2.179 2.174	2.579 2.051	2.361 2.106	3.061 2.110	5.324 2.564
50°C RDA strain sweep (5% strain) tan δ	0.2471 0.2267	--	0.1897 0.1620	0.2083 0.1653	0.2068 0.1595	0.2144 0.1668	0.2723 0.1843
50°C Dynastat tan δ	0.2393 0.2095	--	0.1780 0.1651	0.1999 0.1708	0.1948 0.1609	0.1941 0.1673	0.2493 0.1858

Examples 25-30: *Polymers with octamethylcyclotetrasiloxane intermediate groups*

The procedure described with respect to Examples 6-24 was, in substantial part, repeated. Example 25 was quenched with isopropanol (i.e., no intermediate group), while Examples 26-29 involved reacting a BuLi-initiated SBR with octamethylcyclotetrasiloxane (instead of hexamethyltrisiloxane as in Examples 6-

24) followed by reaction with functional groups (27) 3-aminopropyltrimethoxysilane, (28) [3-(methylamino)propyl]trimethoxysilane, and (29) 1,4-butane sultone. Examples 26-29 were then quenched with isopropanol. Example 30 involved reacting a DAPDT-initiated SBR with octamethylcyclotetrasiloxane followed by reaction with 3-aminopropyl-triethoxysilane, and quenching with isopropanol.

Each polymer was processed and compounded substantially as before. Physical properties of the resulting filled compounds are shown below in Table 7.

Table 7: Testing data from Examples 25-30

	25	26	27	28	29	30
M_n (kg/mol)	97	97	87	90	97	93
M_w / M_n	1.03	1.03	1.23	1.13	1.03	1.15
% coupling	0	0	11.6	10.6	0	10.7
T_g (°C)	-35.6	-35.0	-35.4	-35.8	-35.4	-36.3
Bound rubber (%)	9.8 19.7	10.5 76.7	30.3 83.8	25.3 81.9	11.7 78.3	31.3 84.8
Surfanalyzer D.I.	93.2 76.6	96.1 73.5	94.5 68.1	96.2 67.8	95.8 72.0	97.9 83.7
171°C MDR t_{50} (min)	3.13 7.86	3.01 7.56	2.67 6.92	2.68 6.92	3.10 7.15	2.54 6.22
171°C MH-ML (kg-cm)	17.1 21.6	18.1 14.6	16.3 15.8	16.8 24.8	17.1 15.5	20.2 17.8
ML_{1+4} @ 130°C	19.6 50.5	19.6 83.5	26.5 89.6	24.6 87.7	20.3 83.4	33.3 *N/A*
300% modulus @ 23°C (MPa)	10.3 9.5	10.8 13.3	11.7 *N/A*	10.8 14.7	10.2 14.4	13.6 13.6
Tensile strength @ 23°C (MPa)	14.9 11.9	15.4 13.3	16.4 14.1	16.0 14.1	14.7 13.7	17.3 17.5
Temp. sweep 0°C tan δ	0.217 0.198	0.204 0.268	0.229 0.275	0.207 0.276	0.213 0.279	0.228 0.245
Temp. sweep 50°C tan δ	0.271 0.240	0.260 0.188	0.256 0.180	0.268 0.186	0.263 0.190	0.210 0.150
RDA 0.25-14% ΔG' (MPa)	6.000 8.373	5.510 2.179	2.651 2.143	3.447 2.235	5.104 2.293	2.425 2.136
50°C RDA strain sweep (5% strain) tan δ	0.2955 0.2589	0.2831 0.1820	0.2307 0.1786	0.2512 0.1705	0.2874 0.1840	0.1735 0.1473
50°C Dynastat tan δ	0.2767 0.2187	0.2595 0.1688	0.2057 0.1616	0.2360 0.1562	0.2624 0.1654	0.1602 0.1358

Examples 31-36: *Polymers with cyclohexene oxide intermediate unit*

The procedure described with respect to Examples 6-24 was, in substantial part, repeated. Example 31 was quenched with isopropanol (i.e., no intermediate unit), while examples 32-36 involved reacting a BuLi-initiated SBR with

cyclohexene oxide followed by reaction with a functionalizing agent for Examples 33-36 and quenched as according to Table 8

Table 8: Reaction and termination of Examples 31-36

Example	Intermediate Unit	G_t (Functionalizing Agent)	Quenching Agent
31	N/A	N/A	isopropanol
32	Cyclohexene oxide	N/A	isopropanol
33	Cyclohexene oxide	3-aminopropyltrimethoxysilane	isopropanol
34	Cyclohexene oxide	[3-(methylamino)propyl]trimethoxide	isopropanol
35	Cyclohexene oxide	2-dodecen-1-yl succinic anhydride	isopropanol
36	Cyclohexene oxide	1,2-thioxane-1,1-dioxide	isopropanol

Each polymer was processed and compounded substantially as before. Physical properties of the resulting filled compounds are shown below in Table 9.

Table 9: Testing data from Examples 31-36

	31	**32**	**33**	**34**	**35**	**36**
M_n (kg/mol)	89	90	77	82	95	89
M_w / M_n	1.04	1.04	1.12	1.07	1.08	1.03
% coupling	0	0	30.2	0	11.7	0
T_g (°C)	-33.6	-33.9	-33.6	-33.6	-33.7	-33.4
Bound rubber (%)	9.1 18.3	9.5 23.0	16.7 24.9	15.9 24.5	13.1 22.9	10.5 21.3
Surfanalyzer D.I.	87.8 76.6	90.5 74.1	94.6 78.6	93.7 74.4	94.1 77.9	91.5 72.5
171°C MDR t_{50} (min)	3.27 8.63	3.25 8.12	2.80 8.28	2.94 7.60	2.88 6.37	3.27 8.40
171°C MH-ML (kg-cm)	15.5 20.1	16.5 20.9	16.9 20.5	16.2 21.4	16.9 22.7	15.8 20.5
ML_{1+4} @ 130°C	18.3 47.4	18.5 49.7	20.0 48.3	20.2 47.9	21.3 55.0	18.2 50.3
300% modulus @ 23°C (MPa)	9.7 9.5	10.7 10.1	11.4 9.8	10.9 10.2	11.1 10.4	10.0 9.5
Tensile strength @ 23°C (MPa)	14.3 12.2	15.8 12.5	16.5 11.2	16.4 11.1	17.1 12.2	14.6 11.5
Temp. sweep 0°C tan δ	0.224 0.198	0.228 0.209	0.230 0.202	0.224 0.203	0.225 0.213	0.231 0.231
Temp. sweep 50°C tan δ	0.310 0.247	0.284 0.259	0.281 0.248	0.286 0.241	0.281 0.224	0.287 0.253
RDA 0.25-14% ΔG′ (MPa)	4.691 8.827	5.170 8.807	4.570 8.107	4.656 8.312	4.783 8.410	4.713 8.448
50°C RDA strain sweep (5% strain) tan δ	0.2918 0.2622	0.2878 0.2568	0.2711 0.2621	0.2780 0.2506	0.2669 0.2331	0.2868 0.2540
50°C Dynastat tan δ	0.2745 0.1700	0.2698 0.2385	0.2598 0.1690	0.2668 0.1778	0.2568 0.1871	0.2724 0.1563

Examples 37-42: *Polymers with cyclohexene sulfide intermediate units*

The procedure described with respect to Examples 6-24 was, in substantial part, repeated. Example 37 was quenched with isopropanol (i.e., no intermediate unit), while examples 32-36 involved reacting a BuLi-initiated SBR with

cyclohexene oxide followed by reaction with a functionalizing agent for Examples 39-42, and quenched with isopropanol as according to Table 10.

Table 10: Reaction and termination of Examples 37-42

Example	Intermediate Unit	G_t (Functionalizing Agent)	Quenching Agent
37	N/A	N/A	isopropanol
38	cyclohexene oxide	N/A	isopropanol
39	cyclohexene oxide	3-aminopropyltrimethoxysilane	isopropanol
40	cyclohexene oxide	2-dodecen-1-yl succinic anhydride	isopropanol
41	cyclohexene oxide	1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane	isopropanol
42	cyclohexene oxide	1,2-thioxane-1,1-dioxide	isopropanol

Each polymer was processed and compounded substantially as before. Physical properties of the resulting filled compounds are shown below in Table 11.

Table 11: Testing data from Examples 37-42

	37	38	39	40	41	42
M_n (kg/mol)	96	103	103	100	102	70
M_w / M_n	1.03	1.10	1.10	1.08	1.10	1.22
% coupling	0	15.3	16.4	10.1	14.6	43.5
T_g (°C)	-35.7	-36.1	-36.7	-36.2	-35.3	-36.0
Bound rubber (%)	0 2.9	18.5 10.3	30.4 22.4	17.8 23.0	20.8 31.9	27.8 14.7
Surfanalyzer D.I.	93.9 68.4	92.5 70.9	97.1 71.1	92.6 92.9	94.2 75.6	97.5 59.1
171°C MDR t_{50} (min)	3.01 7.91	2.84 7.26	2.63 6.56	2.47 6.13	2.93 6.27	3.14 8.18
171°C MH-ML (kg-cm)	16.6 20.9	16.8 22.7	16.2 22.6	16.1 22.4	16.6 21.9	17.0 16.8
ML_{1+4} @ 130°C	18.9 56.3	29.9 66.7	31.6 67.5	29.5 68.1	29.5 69.2	28.9 79.4
300% modulus @ 23°C (MPa)	9.5 9.4	11.4 10.9	11.7 11.1	11.3 10.4	11.8 9.8	10.2 9.0
Tensile strength @ 23°C (MPa)	15.3 12.6	15.6 14.9	15.7 14.2	16.2 14.2	15.5 13.7	15.5 13.9
Temp. sweep 0°C tan δ	0.207 0.174	0.218 0.188	0.223 0.193	0.228 0.181	0.219 0.193	0.210 0.191
Temp. sweep 50°C tan δ	0.278 0.225	0.249 0.219	0.256 0.224	0.237 0.213	0.234 0.219	0.267 0.219
RDA 0.25-14% ΔG' (MPa)	5.817 8.183	2.543 6.667	2.072 5.977	2.103 6.863	1.539 5.333	3.271 4.263
50°C RDA strain sweep (5% strain) tan δ	0.2849 0.2595	0.2182 0.2306	0.2063 0.2122	0.2090 0.2106	0.1848 0.2173	0.2441 0.2215
50°C Dynastat tan δ	0.2695 0.2338	0.2053 0.2031	0.2004 0.2018	0.1993 0.2015	0.1716 0.2021	0.2261 0.2055

Examples 43-48: *Polymers with butylene oxide intermediate unit*

The procedure described with respect to Examples 6-24 was, in substantial part, repeated. Example 43 was quenched with isopropanol (i.e., no intermediate unit), while examples 44-48 involved reacting a BuLi-initiated SBR with

cyclohexene oxide followed by reaction with a functionalizing agent for Examples 45-48, and quenched with isopropanol as according to Tabe 12.

Table 12: Reaction and termination of Examples 43-48

Example	Intermediate Unit	G_t (Functionalizing Agent)	Quenching Agent
43	N/A	N/A	isopropanol
44	cyclohexene oxide	N/A	isopropanol
45	cyclohexene oxide	3-aminopropyltrimethoxysilane	isopropanol
46	cyclohexene oxide	[3-(methylamino)propyl]trimethoxysilane	isopropanol
47	cyclohexene oxide	2-dodecen-1-yl succinic anhydride	isopropanol
48	cyclohexene oxide	1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane	isopropanol

Each polymer was processed and compounded substantially as before. Physical properties of the resulting filled compounds are shown below in Table 13.

Table 13: Testing data from Examples 43-48

	43	44	45	46	47	48
M_n (kg/mol)	96	98	91	92	98	99
M_w / M_n	1.04	1.03	1.08	1.05	1.03	1.04
% coupling	0	0	6.4	3.2	1.8	3.1
T_g (°C)	-36.1	-35.9	-35.5	-36.1	-35.8	-35.5
Bound rubber (%)	8.3 12.3	9.0 14.5	14.5 19.5	5.9 15.6	7.9 15.7	9.4 15.2
Surfanalyzer D.I.	94.7 22.9	95.1 22.4	97.5 28.1	95.4 24.3	95.3 24.8	98.6 23.6
171°C MDR t_{50} (min)	2.88 7.02	3.00 6.90	2.63 6.52	2.59 5.78	2.89 6.29	2.93 6.94
171°C MH-ML (kg-cm)	16.6 18.4	16.5 19.6	16.5 18.9	16.6 20.8	16.5 19.8	16.7 19.3
ML_{1+4} @ 130°C	20.0 39.2	21.0 40.4	22.2 41.2	20.8 *N/A*	20.3 40.9	20.4 40.9
300% modulus @ 23°C (MPa)	10.2 8.5	9.9 9.8	10.5 10.4	10.5 11.5	10.3 9.1	10.4 9.9
Tensile strength @ 23°C (MPa)	15.3 11.4	16.2 12.7	16.4 13.3	15.2 13.9	16.7 11.3	17.2 12.1
Temp. sweep 0°C tan δ	0.202 0.193	0.211 0.197	0.202 0.201	0.212 0.205	0.213 0.193	0.212 0.198
Temp. sweep 50°C tan δ	0.261 0.257	0.274 0.258	0.265 0.263	0.271 0.257	0.261 0.241	0.270 0.252
RDA 0.25-14% ΔG' (MPa)	5.395 8.063	4.820 7.646	4.507 4.198	4.911 7.669	4.392 6.918	5.190 7.670
50°C RDA strain sweep (5% strain) tan δ	0.2764 0.2653	0.2818 0.2570	0.2729 0.2357	0.2815 0.2386	0.2730 0.2216	0.2870 0.2458
50°C Dynastat tan δ	0.2572 0.2421	0.2627 0.2322	0.2506 0.2279	0.2574 0.2288	0.2538 0.2211	0.2584 0.2310

CLAIMS

We claim:

1. A functionalized polymer comprising:

a) an elastomer,

b) a terminal functional group comprising at least one heteroatom, and

c) an intermediate unit, between said elastomer and said functional group, said intermediate unit comprising a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion.

2. The functionalized polymer of claim 1 wherein said terminal functional group comprising said at least one heteroatom comprises derivation from a primary or secondary amine.

3. The functionalized polymer of claim 1 wherein said intermediate unit comprises derivation from the ring opening of a cyclic structure that comprises a heteroatom.

4. A method of making a functionalized polymer, comprising:

a) providing a polymer that comprises, at the living end, a unit comprising a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion; and

b) reacting the polymer with a compound comprising at least one heteroatom.

5. The method of claim 4 wherein said compound comprising at least one heteroatom comprises a primary or secondary amine.

6. The method of claim 4 wherein the intermediate unit comprises derivation from the ring opening of a cyclic structure that comprises a heteroatom.

7. A composition comprising at least one reinforcing filler and a functionalized polymer of the general formula

$$E\text{-}A\text{-}G_t$$

wherein

E is an elastomer,

G_t is a terminal functional group comprising at least one heteroatom, and

A is a unit comprising a terminal moiety which, in its anionic form, comprises less basic than a secondary amino radical ion.

8. The composition of claim 7 wherein G_t comprises a primary or secondary amine radical.

9. The composition of claim 7 wherein A comprises a radical of a cyclic structure that comprises a heteroatom.

10. A method of making a tire tread composition comprising blending at least one reinforcing filler and a functionalized polymer of the general formula

$$E\text{-}A\text{-}G_t$$

wherein

E comprises an elastomer,

G_t comprises a terminal finctional group comprising at least one heteroatom and

A comprises an intermediate unit comprising a terminal moiety which, in its anionic form is less basic than a secondary amino radical ion

11. The method of claim 10 wherein said at least one reinforcing filler comprises at least one of carbon black and silica.

12. The method of claim 10 wherein said A comprises derivation from the ring opening of a cyclic structure that comprises a heteroatom.

13. A tire tread composition comprising at least one reinforcing filler and a functionalized polymer of the general formula

$$E\text{-}A\text{-}G_t$$

wherein

E comprises an elastomer,

G_t comprises a terminal finctional group comprising at least one heteroatom, and

A comprises an intermediate unit comprising a terminal moiety which, in its anionic form is less basic than a secondary amino radical ion.

14. The tire tread composition of claim 13, wherein the said at least one reinforcing filler comprises at least one of carbon black and silica.

15. The tire tread composition of claim 13 further comprising at least one of an additive and a processing aid.

16. A tire comprising a tread comprising the tire tread composition of claim 15.

17. A method of making an amine-functionalized polymer, comprising:

a) in a reaction medium, reacting a living polymer with a cyclic compound comprising at least one heteroatom so as to provide an intermediate functionalized living polymer comprising an anionic charge on said heteroatom where the resulting anion is less basic than a secondary amino radical ion;

b) reacting said intermediate functionalized living polymer with an amine comprising an active hydrogen atom attached to the amino nitrogen atom of said amine.

18. The method of claim 17 wherein said cyclic compound comprising at least one heteroatom comprises a polysiloxane.

19. The method of claim 18 wherein said polysiloxane comprises hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane.

20. The method of claim 17 wherein said cyclic compound comprising at least one heteroatom comprises an epoxide or an episulfide.

21. A composition comprising a silica reinforcing filler and a polymer comprising an elastomer and a terminal moiety, wherein said terminal moiety in its anionic form, is less basic than a secondary amino radical ion.

22. The composition of claim 21, wherein said terminal moiety derived from a ring opening of a cyclic compound comprising at least one heteroatom.

23. The composition of claim 22, wherein said cyclic compound comprises a polysiloxane.

24. The composition of claim 23, wherein said polysiloxane comprises hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane.

25. A tire comprising a tread comprising the composition of claim 21.

ABSTRACT

A functionalized polymer includes an elastomer, a terminal functional group including at least one heteroatom, and an intermediate unit between the elastomer and the functional group; the intermediate unit includes a terminal moiety which, in its anionic form, is less basic than a secondary amino radical ion. Methods of making the functionalized polymer and of using it with particulate filler to make, e.g., a tire tread composition also are disclosed.

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